this process the sulfites are partially removed by precipitation as the calcium salt. The liquor is then concentrated and fermented by a special sulfur-resisting yeast. The method here given, however, appears to have several advantages over the Ekström process.

On the whole, the above described process appears to be sound. The reactions brought about are definite, simple and easily controlled.

CONCLUSIONS

1—A simple and easily controlled process has been proposed for the economic production of alcohol from waste sulfite liquor.

2—The process also detoxicates the sulfite liquor so as to make it, when diluted in the usual amount, practically harmless to fish.

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THE USE OF COPPER OXIDE FOR FRACTIONATION COMBUSTION OF HYDROGEN AND CARBON MONOXIDE IN GAS MIXTURES

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The purpose of this paper is to record the authors' experience in using copper oxide for the determination of hydrogen and carbon monoxide in gas mixtures. The method had given us much better satisfaction than methods that demand the use of acid or ammoniacal solutions of cuprous chloride for determining carbon monoxide, or of palladium asbestos, palladium sponge, or colloidal palladium solution for determining hydrogen. It is believed that this method should be more widely used than it is.

In the use of copper oxide the oxygen for the combustion comes from the reagent itself. After it has been used for a time some red cuprous oxide begins to show or even some completely reduced copper. It is then necessary to heat it and pass air over it, when it is again ready for use.

A great advantage of the method over the use of absorbents for carbon monoxide and hydrogen is the elimination of the preparation of solutions and the fact that copper oxide does not become poisoned as at times do some palladium preparations that are used for the hydrogen determination.

Cuprous-chloride solutions for the carbon monoxide determination are somewhat tedious to prepare and have a small absorption capacity. In addition, two solutions have to be used for precise work. Copper oxide, on the other hand, lasts for practically an indefinite number of determinations, and is easily restored to activity when partly reduced by drawing air over it when hot.

Jäger² was the first to use copper oxide for the fractional combustion of hydrogen in the presence of methane. He found that hydrogen was completely burned when passed over copper oxide kept at a temperature of 250° C. The tube containing the copper oxide was surrounded by an oven heated with a gas

flame. Jäger recommended that next the methane be burned by heating the tube containing the copper oxide to bright redness. Knorre,¹ in using the method, replaced the soft glass used by Jäger, by one made of transparent quartz. L. Uebbelohde and de Castro² also used a quartz tube for holding the copper oxide: the tube was surrounded by an asbestos oven: they used a temperature of 270° C. for burning the hydrogen and copper oxide and a red heat for burning paraffin hydrocarbons.

E. Terres and E. Manguin³ state that hydrogen is burned completely at 250° to 300° C. They found that dry carbon monoxide by itself in the dry state is only 90 to 94 per cent burned at 300° C.; also that even when hydrogen was mixed with acetylene and ethylene the latter did not burn completely because of the deposition of carbon on the copper oxide. They add further that benzene resembles ethylene as regards completeness of combustion, and that methane begins to burn at 310° C., the temperature being lowered a few degrees, however, by the presence of hydrogen, and is completely burned at a red heat. The oxidation of dry carbon monoxide began at 145° C., and of wet carbon monoxide below 100° C., but was not complete at 310° C. Hydrogen began to oxidize at 160° to 170° C. and at 250° C. the oxidation was complete. Carbon monoxide burned completely, however, in the presence of sufficient hydrogen at 300° C.

J. G. Taplay⁴ uses a temperature of 270° C. for hydrogen and 850° C. for the paraffin hydrocarbons. S. H. Worrell⁵ confines the copper oxide in a silica tube of 1/4-in. bore and 7 in. long, and heats it with a gas flame. He states that copper oxide passing an 80-mesh sieve should not be used. A temperature of 250 to 260° C. is used by him for burning hydrogen and carbon monoxide, and red heat for methane.

Dennis⁶ confines the copper oxide in a soft glass tube and burns the hydrogen and carbon monoxide together at 270° C., but prefers to burn paraffin hydrocarbons, if present in the gas mixture, by means of a platinum spiral in a Dennis combustion pipette. His chief objection to the method of determining methane with copper oxide lies in the fact that prolonged heating of the combustion tube to a high temperature and repeated passage of the gas through it are necessary for the complete oxidation of the methane."

Wibaut⁷ mixes cerium oxide with the copper oxide in sufficient quantity to produce a grayish white mixture with the latter. He states that the combustion is made more rapid by this means.

Taylor⁸ heats the copper oxide in a glass tube by means of a small electric furnace. The hydrogen and carbon monoxide are burned at a temperature of 275° C. for gases in which the average value of n in C_nH_{2n+2} is as high as 1.65, and paraffin hydrocarbons are burned with oxygen by means of a heated platinum

¹ *Chem. Ztg.*, **33** (1909), 717.

² *J. Gasbel.*, **54** (1911), 810-814.

³ *Ibid.*, **58** (1915), 8-11.

⁴ *J. Gas Lighting*, **118** (1912), 217, 285.

⁵ *Mel. Chem. Eng.*, **11** (1913), 245-247.

⁶ L. M. Dennis, "Gas Analyses," **1913**, pp. 198-206.

⁷ *Chem. Weekblad*, **11** (1914), 498.

⁸ *Jour. Soc. Chem. Ind.*, **6** (1914), 845.

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² *J. Gasbel.*, **41** (1898), 764.

spiral. He says the exact temperature that can be used will depend upon the nature of the hydrocarbons present, and that with methane only, 300°C . is probably not too high, but at this temperature there is danger of oxidation of the higher homologs of methane. Tests by Taylor also showed that not only may hydrogen and carbon monoxide be burned in the presence of methane without danger of oxidation of the latter but also in the presence of high concentrations of higher paraffins. He states that the time required for the complete burning of the hydrogen and carbon monoxide does not seem to be a function of the quantities present as much as the nature of the gas mixture. For ordinary illuminating gas he found that the hydrogen is usually completely removed in 6 to 10 slow passes over the copper oxide. With some low-temperature coal distillates, not scrubbed, there were required as high as 40 minutes to remove 3 to 5 cc. Taylor concludes that, in general, when the contraction due to the burning of the hydrogen has ceased, the carbon monoxide may be assumed to have been completely oxidized, unless it be present in much greater concentration than the hydrogen, in which case passage through the copper oxide should be continued some minutes longer.

Nemselow¹ uses a temperature of 250°C . He found that silver oxide could also be used, although it is not as practical.

EXPERIMENTAL

The apparatus with which the authors performed their work is shown in Fig. I. The burette *a* has a capacity of 100 cc. and is graduated in 0.1 cc.; an attachment, *j*, *n*, compensates for outside changes of temperature and pressure during the course of the analysis; *h* and *i* are three-way stop-cocks; *b* contains caustic potash solution for the removal of carbon dioxide; *c*, fuming sulfuric acid for removing unsaturated hydrocarbons; *d*, alkaline pyrogallate solution for removing oxygen; *e* is a slow-combustion pipette containing an electrically heated platinum spiral. This coiled spiral is $4\frac{1}{2}$ in. long and No. 30 B. & S. gauge. The glass tubes supporting the spiral are filled with mercury. The latter acts as electrical contacts between the ends of the platinum spiral and the platinum wires sealed into the bottom of each tube. The ends of the platinum spiral are fused to the inside of the open glass tubes at the top. Thus fastened and with the ends of the spiral dipping into the mercury, they always stay in place. A current of about 4 to 4.5 amperes at 6.2 volts is used to raise the wire to a white heat for burning the paraffin hydrocarbons. Mercury is used in this pipette, also in the burette; *f* is a glass tube (inside diameter, 4 mm.) containing the copper oxide, surrounded by an electrically heated oven, *g*,² which is supported by a standpipe, by means of which it can be raised from the copper oxide tube when not in use. Copper oxide that passes a 100-mesh sieve is not used in the tube. One U-tube used by the authors for holding copper oxide contained 3.3 grams and a free space volume of 1.89 cc.

¹ *Z. anal. Chem.*, **48** (1909), 232-272.

² Similar to the one used by Taylor (*loc. cit.*).

In Fig. I, *o* and *p* are three-way T stop-cocks, so that the gas can be passed either through the branch *o*, *p* into the pipette *d* or through the copper oxide tube and thence into the pipette *e*. The bulbs *m* and *l* slide up and down on two standpipes (not shown). A simpler burette is shown at *l*, in case it is desired to use water in the burette instead of mercury.

USE OF THE APPARATUS SHOWN IN FIG. I

There follows the method of making an analysis of a gas mixture containing carbon dioxide, unsaturated hydrocarbons (principally ethylene), oxygen, carbon monoxide, methane, ethane, hydrogen and nitrogen.

Before proceeding with the analysis the capillary train and U tube are swept free of oxygen or residual gases from a previous determination by drawing a sample of air into the burette and passing it into the alkaline pyrogallate pipette *d* to remove oxygen. The residual nitrogen is then passed into all the pipettes and through the CuO tube to sweep out other gases

FIG. I.—COMPLETE GAS ANALYSIS APPARATUS INCLUDING COPPER OXIDE TUBE

(usually oxygen) that may have been contained therein. Instead of extracting nitrogen from the air for this purpose each time, a supply of nitrogen may be kept on hand. The electric current is then turned through the oven. Preliminary trials will have shown the current strength demanded. The ovens in use by the authors require about 2.4 amperes at 30 volts. Connection is made through regulating resistances to the 220 volt lighting circuit of the building through a lamp bank rheostat. The current is switched on at the beginning of an analysis so that the oven will be heated to the desired temperature (275° to 300°C .) by the time the analyst is ready to make the fractional combustion analysis.

Some of the gas mixture is then drawn into the burette, measured and passed into the pipettes *b*, *c* and *d*, for the removal of carbon dioxide, illuminants and oxygen. After the percentage of these constituents

has been recorded, the stop-cocks *o*, *p* and *s* are turned so that communication is made between the burette and the pipette *e*, through the copper oxide tube. By this time the latter will have reached the desired temperature. The furnace is next lowered over the copper oxide tube and the gas mixture slowly passed back and forward through it between the burette and slow-combustion pipette *e* until no further diminution in volume is noted by reading the gas volume in the burette. The authors have found that a maximum of about 15 minutes is required to burn completely the carbon monoxide and hydrogen in various gas mixtures. Carbon monoxide burns readily in the presence of hydrogen, but much more slowly when burned alone. After combustion is complete the electric oven is raised from the copper-oxide tube and the latter allowed to cool. The authors hasten the cooling by playing a blast of cold air from a compressed air pipe on the tube: this operation requires about 5 minutes. A safe way is to make a second reading of the gas volume after a few minutes' time to make sure that no further contraction, due to cooling, takes place. Next the carbon dioxide is removed by passing the gas mixture into pipette *b* (the KOH pipette). Gas in the train and copper-oxide tube containing carbon dioxide is swept into the KOH pipette by raising and lowering the level bulb *m*, with stop-cocks *s*, *p*, *o* and *x* open.

After the hydrogen and carbon monoxide have been determined, the residual gas is passed into the KOH pipette *b* for storage and the stop-cock closed. Enough oxygen to burn the paraffin hydrocarbons is

TABLE I—ANALYSIS (BY CuO METHOD) OF GAS FROM COAL DISTILLATION

	No. 1 cc.	No. 2 cc.	Percentage No. 1	Percentage No. 2
Volume of sample taken.....	40.2	41.5	..	..
Volume after KOH absorption.....	39.6	40.9	..	..
Carbon dioxide (CO ₂) absorbed.....	0.6	0.6	1.5	1.5
Volume after fuming sulfuric acid absorption.....	39.3	40.7	..	..
ILLUMINANTS, etc., absorbed.....	0.3	0.2	0.7	0.5
Volume after alkaline pyrogallate absorption.....	39.3	40.7	..	..
Oxygen absorbed (O ₂).....	0.0	0.0	0.0	0.0
Volume after CuO burning.....	26.1	27.0	..	..
Hydrogen in sample (H ₂).....	13.2	13.7	32.8	33.0
Volume after KOH absorption.....	23.8	24.6	..	..
Carbon monoxide in sample (CO).....	2.3	2.4	5.7	5.8
Volume taken for slow combustion.....	23.8	24.6	..	..
Oxygen added.....	92.7	92.2	..	..
Total volume.....	116.5	116.8	..	..
Volume after burning.....	69.1	68.0	..	..
Contraction due to burning.....	47.4	48.8	..	..
Volume after KOH absorption.....	45.2	23.3	..	..
Carbon dioxide absorbed.....	23.9	24.7	..	..
Methane in sample (CH ₄).....	23.3	23.9	58.0	57.6
Ethane in sample (C ₂ H ₆).....	0.3	0.4	0.7	1.0
Nitrogen in sample (by difference).....	..	..	0.6	0.6

then drawn into the burette, measured and passed into the slow-combustion pipette *e* (not through the U-tube *f*), and the platinum spiral therein heated to almost a white heat. Next the residual gas is withdrawn from the pipette *b* into the burette and from there slowly passed, at the rate of about 10 cc. per minute, into the pipette *e*. Slow combustion between the oxygen and combustible residual gas therein takes place as fast as the oxygen enters and an accumulation of the mixture necessary for an explosion cannot take place.¹ Only enough of the residual gas should be taken for the final combustion analysis so that there will be an excess of oxygen for the com-

¹ To protect the operator from possible accident, the combustion pipette *e* should be surrounded with a wire gauze.

bustion. In case of doubt a final determination of oxygen by means of the alkaline pyrogallate solution in pipette *d* can be made. After combustion is complete the resulting contraction and carbon dioxide are measured and the gas mixture again passed into the slow-combustion pipette and burned again. There always results further slight contraction and a small amount of carbon dioxide.

Table I gives the observed data of the analysis of a sample of gas collected from coal distillation at high pressures and temperatures.¹

Table II shows analyses of two samples of gas. In one case the carbon monoxide and hydrogen were determined by burning them with copper oxide, and in the other case the carbon monoxide was absorbed by means of ammoniacal cuprous chloride solution and the hydrogen by colloidal palladium solution.²

TABLE II—PERCENTAGE ANALYSES OF A SAMPLE OF GAS BY TWO METHODS

	SAMPLE 1 Colloidal palladium and cuprous chloride		SAMPLE 2 Colloidal palladium and cuprous chloride	
	Method	CuO	Method	CuO
CO ₂	0.2	0.4	0.0	0.0
C ₂ H ₄ , etc.....	44.6	44.6	12.7	12.5
O ₂	1.7	1.6	0.2	0.2
CO.....	0.8	0.9	1.0	0.8
H ₂	7.7	6.7	42.3	42.2
CH ₄	26.4	26.4	41.2	41.1
C ₂ H ₆	11.4	11.2	0.0	0.0
N ₂	7.2	8.2	2.6	3.2

Table III shows two analyses of the same sample. One was made by burning the hydrogen and carbon monoxide over copper oxide with the apparatus shown in Fig. I. The other was made by burning the carbon monoxide, hydrogen and methane together (triple combustion) and a slow-combustion pipette of a Hal-dane gas-analysis apparatus. With the latter, gas volumes as small as 0.002 cc. could be measured.

TABLE III—PERCENTAGE ANALYSES BY COPPER OXIDE AND BY TRIPLE COMBUSTION

ANALYSIS BY	CO ₂	C ₂ H ₄ , etc.	O ₂	H ₂	CO	CH ₄	N ₂
Copper oxide.....	3.9	0.0	15.5	0.0	0.3	0.9	79.4
Triple combustion.....	3.90	0.00	15.46	0.02	0.17	0.84	79.61

Next a gas mixture was prepared containing 4 per cent each of hydrogen, carbon monoxide and methane, and 88 per cent air. Analysis No. 1 shows the results obtained by burning the hydrogen and carbon monoxide at a temperature of 290° C. and methane at a temperature of 800° C. The copper-oxide tube was made of quartz. Analysis No. 2 shows the results obtained by absorbing the carbon monoxide with cuprous chloride, the hydrogen by colloidal palladium, and the methane in a slow-combustion pipette with a hot platinum spiral.

TABLE IV—PERCENTAGE ANALYSES OF A SAMPLE OF GAS BY TWO DIFFERENT METHODS

No.	ANALYSES BY	CO	H ₂	CH ₄
1	Copper oxide.....	3.8	3.6	4.2
2	Cuprous chloride, colloidal palladium and hot spiral.....	4.1	4.0	4.0

Next a mixture of hydrogen (50 per cent) and natural gas³ (50 per cent) was prepared. No. 1 analysis was made by burning the hydrogen with copper oxide and the methane with a hot platinum spiral (slow combustion).

¹ The copper oxide was heated to 290° C. in this and other analyses that follow in determining hydrogen and carbon monoxide. Temperatures ranging from 275° to 300° were found to work satisfactorily.

² THIS JOURNAL, 6 (1914), 992.

³ Containing 84.7 per cent CH₄, 9.4 per cent C₂H₆, 3.0 per cent C₃H₈, 1.3 per cent C₄H₁₀, 1.6 per cent N₂.

No. 2 was made by absorbing the hydrogen with colloidal palladium solution and burning the methane with a hot platinum spiral.

TABLE V—PERCENTAGE ANALYSES OF A MIXTURE OF NATURAL GAS AND HYDROGEN BY TWO DIFFERENT METHODS

No.	ANALYSES BY	H ₂	Natural gas
1	Copper oxide and slow combustion.....	50.7	48.3
2	Colloidal palladium and slow combustion....	50.2	48.1

The above analyses showed that the paraffin hydrocarbons higher than methane were not oxidized, at least in any significant amount, by the copper oxide.

Lastly, there is shown work upon the analysis of the artificially mixed coal and water gas of Pittsburgh. The first analysis was made by burning the carbon monoxide and hydrogen with copper oxide at about 290° C. and paraffin hydrocarbons in the slow-combustion pipette with a hot platinum spiral. The second analysis was made by using copper oxide at about 290° C. to burn the carbon monoxide, a solution of colloidal palladium to absorb the hydrogen, and a hot platinum spiral to burn the paraffin hydrocarbons. The third analysis was made by burning carbon monoxide and hydrogen at about 290° C. with copper oxide and by burning the paraffin hydrocarbons at a red heat with copper oxide.

TABLE VI—PERCENTAGE ANALYSES OF THE ARTIFICIAL ILLUMINATING GAS OF PITTSBURGH

No.	CO ₂	Illuminants	O ₂	CO	H ₂	CH ₄	C ₂ H ₆	N ₂	TOTAL
1.....	2.5	7.4	0.4	11.5	43.6	30.6	2.1	1.9	100.0
2.....	2.6	7.0	0.4	11.7	43.9	30.7	2.2	1.5	100.0
3.....	2.4	7.5	0.4	11.5	43.4	30.4	2.2	2.2	100.0

SUMMARY

I—The authors' experience with the copper-oxide method, devised by Jäger for the fractional combustion of hydrogen and carbon monoxide, is described.

II—A gas-analysis apparatus, embodying a copper-oxide tube somewhat different in form from others on the market, but containing no new principle, is also described.

III—A temperature of the copper oxide of between 275° and 300° is adapted for burning hydrogen and carbon monoxide in a wide variety of mixtures. Most previous experimenters have adopted temperatures in this range.

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A NEW ACCURATE METHOD OF GAS ANALYSIS

By O. A. KRONE

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Figs. I and II show the apparatus used for estimating the quantities of carbon dioxide, illuminants, oxygen, carbon monoxide, methane, ethane, hydrogen and nitrogen in gaseous mixtures.

B, B₁ are 100 cc. burettes graduated the entire length in 0.1 cubic centimeter. C, C₁ are water jackets for the burettes. D is a three-way glass Geissler cock of 2 mm. bore. E, E₁ are bent capillary tubes of 1 mm. bore. F is a three-way Geissler cock, G is a two-way cock having a T capillary fused to F. H is a bent 1.5 mm. bore capillary, whose orifice, H₁, is melted to measure 0.3 mm. I is a piece of glass tubing having walls of sufficient strength, and an internal diameter of 1.75 cm. drawn down to a

capillary of 1.5 mm. internal diameter. J is the brass body holding the combustion tube. K is a three-way glass cock of 2 mm. bore. N is a two-way glass cock of 5 mm. bore. P is a glass-covered pipette stand whose height is adjustable. Q is a set screw for adjustment of P. J, the brass body holding the combustion tube, has two small holes, a little smaller than 1.5 mm. diameter, drilled from the posterior side into 1/3 of the body J. Into these are fitted the two legs of a platinum combustion tube of 1.5 mm. outside and 0.5 mm. inside diameter. The small holes are 1 cm. apart. The platinum tube is about 10 to 11 cm. long and is bent to form a U, the two legs of which run parallel about 1 cm. apart. Into the forepart of the body two large holes, about 8 mm. in diameter, are drilled, whose centers meet the centers of the 1.5 mm. holes drilled from the rear.

The brass body has grooves milled in large enough to have a water circulation to keep the rubber tubing cool, which holds the bent glass capillaries of 1.5 mm. bore fitting tightly into the larger holes A, A. These

FIG. I—ARRANGEMENT OF APPARATUS

W, a 4 liter bottle for storing oxygen over water, is connected to bottle Y of the same size placed above it to keep the oxygen under pressure

glass capillaries are bent so that the combustion tube protrudes in the rear of the apparatus. Around the brass body is soldered a piece of sheet copper to form a cup for water. The platinum tube is then soldered in, gas-tight.

If mercury is used as the confining fluid in burette B, the platinum tube is either brazed or silvered in, gas-tight. The ends of the platinum tube are tapered so that tight joints are secured by forcing the ends into the brass body.

A small piece of asbestos paper is fitted onto the platinum capillary to prevent the unused heat from softening the solder.

A Méker or Bausch and Lomb high temperature burner is used to heat the tube and is adjusted to position with an iron clamp fastened to the apparatus support. All rubber connections should be made with the best heavy-walled rubber tubing which should be of small enough size to give a tight joint.

All glass capillaries should fit shoulder to shoulder